Understanding Inherent Substrate Selectivity during Tungsten ALD: Effect of Surface Preparation, Hydroxyl Density and Metal Oxide Composition on Nucleation Mechanisms

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Area-selective thin film deposition is expected to be important for advanced sub-10 nanometer semiconductor devices, enabling feature patterning, alignment to underlying structures and edge definition. Several atomic layer deposition (ALD) processes show inherent propensity for substrate-dependent nucleation. This includes tungsten ALD which is more energetically favorable on Si than on SiO₂, but selectivity is often lost after several ALD cycles. We investigated the causes of tungsten nucleation on SiO₂ and other “non-growth” surfaces during the WF₆/SiH₄ ALD process to determine how to expand the “selectivity window.” We suggest that hydroxyls generated during the piranha clean act as nucleation sites and show that excluding the piranha clean or heating samples following the piranha clean extends the tungsten selectivity window. Quartz crystal microbalance (QCM) analysis shows that more “basic” oxide surfaces such as Al₂O₃ show faster tungsten nucleation than “acidic” oxides like SiO₂ or TiO₂, likely because of the difference in hydroxyl concentration. The selectivity window is extended by exposing the substrate to a metal oxide ALD precursor prior to tungsten deposition. We reason that the inorganic reactant reacts and effectively removes available hydroxyl groups that would act as tungsten nucleation sites. Finally we assess how the tungsten ALD precursors interact with the hydroxyl sites though pre-exposures of the WF₆ and SiH₄ prior to tungsten ALD deposition. Our results show a clear correlation between SiH₄ exposure time and the resulting tungsten nucleation on SiO₂.

Figure 1. QCM analysis of the SiH₄/WF₆ tungsten ALD process at 220°C on oxide and TiCl₄−modified surfaces.